

**NASA TECHNICAL  
MEMORANDUM**

**NASA TM X-53807**

December 26, 1968

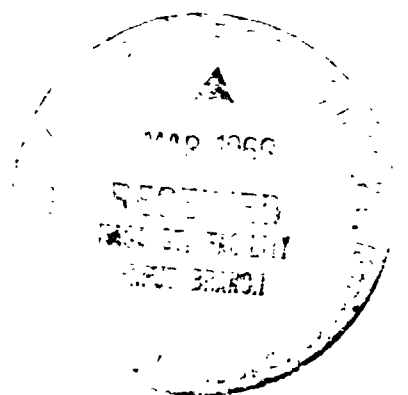
NASA TM X-53807

**COMPATIBILITY OF METALS WITH HYDROGEN**

By C. E. Cataldo  
Propulsion and Vehicle Engineering Laboratory

FACILITY FORM 602

N 60-19002	
(ACCESSION NUMBER)	
94	
(PAGES)	
TMX 53807	
(NASA CR OR TMX OR AD NUMBER)	
	1 (THRU)
	(CODE)
	17 (CATEGORY)



**NASA**

*George C. Marshall Space Flight Center  
Marshall Space Flight Center, Alabama*

TECHNICAL MEMORANDUM X- 53807

COMPATIBILITY OF METALS WITH HYDROGEN

By

C. E. Cataldo

George C. Marshall Space Flight Center  
Marshall Space Flight Center, Alabama

ABSTRACT

This report summarizes three different but related categories of hydrogen embrittlement problems encountered in various components of Saturn launch vehicle hardware. The status of research programs, established to investigate these failure mechanisms and solutions to prevent failures, is presented. Corrective actions taken to minimize failures from high pressure hydrogen effects, the formation of hydrides in titanium, and hydrogen absorption through various metals processing techniques are described.

NASA - GEORGE C. MARSHALL SPACE FLIGHT CENTER

NASA - GEORGE C. MARSHALL SPACE FLIGHT CENTER

---

TECHNICAL MEMORANDUM X- 53807

---

COMPATIBILITY OF METALS WITH HYDROGEN

By

C. E. Cataldo

PROPULSION AND VEHICLE ENGINEERING LABORATORY  
RESEARCH AND DEVELOPMENT OPERATIONS

## TABLE OF CONTENTS

	Page
SUMMARY . . . . .	1
INTRODUCTION . . . . .	1
THE EFFECT OF HIGH PRESSURE HYDROGEN ON VARIOUS METALS. . . .	2
EMBRITTLEMENT OF TITANIUM BY THE FORMATION OF TITANIUM HYDRIDE . . . . .	5
HYDROGEN EMBRITTLEMENT FROM VARIOUS CLEANING, PICKLING, AND ELECTROPLATING PROCESSES . . . . .	7
DISCUSSION . . . . .	9
NASA CORRECTIVE ACTIONS . . . . .	11
CONCLUSION . . . . .	12
REFERENCES . . . . .	14

## LIST OF TABLES

Table	Title	Page
I	Arrangement of Materials in Order of Percent Reduction of Notch Strength in 10,000 psi Hydrogen . . . . .	15
II	Materials not Susceptible to Hydrogen Embrittlement by Electroplating, or Pickling . . . . .	15
III	Metals Susceptible to Hydrogen Embrittlement . . . . .	16
IV	Thermal Treatments for Hydrogen Embrittlement Relief . . . . .	16

## LIST OF ILLUSTRATIONS

Figure	Title	Page
1	Sketch of Multiple Layer Construction for Pressure Vessel . . . . .	17
2	Half Sphere of Fractured Titanium Helium Bottle . . . . .	18
3	Hydride Formation in Ti-6Al-4V Welded with C.P. Filler Wire . . . . .	19
4	Cross-Section of Threaded Segment of Pressure Bottle and Cross-Section of Threaded Area . . . . .	20

## TECHNICAL MEMORANDUM X-53807

### COMPATIBILITY OF METALS WITH HYDROGEN

#### SUMMARY

A considerable number of launch vehicle component and associated ground support equipment failures have occurred due to embrittlement by hydrogen. In the case of ground support equipment, problems have been attributed primarily to high pressure gas storage, wherein large steel storage tanks are used for supplying gas for various vehicle systems requirements. Titanium pressure vessels have failed due to the formation of a brittle titanium hydride phase in weldments. A large number of components, particularly high strength alloy steels used in fasteners and other hardware, have been embrittled due to the absorption of hydrogen during electroplating or chemical cleaning processes. Various research programs have been instituted to study the mechanisms associated with the embrittlement reactions. Although basic mechanisms have not been identified in most cases, much has been learned about relative susceptibility of various classes of materials to embrittlement and sufficient knowledge has been gained to allow one to make a better selection of material or to refine processes to minimize the dangers of embrittlement for most service conditions encountered. There are considerable gaps in the data available; essentially, no thresholds have been established for specific influences such as pressure, temperature, and stress, much less the influence of combined factors.

#### INTRODUCTION

During the development and early flights of the Saturn family of launch vehicles, failures have been encountered in a variety of components, including flight hardware and ground support equipment, that have been attributed to hydrogen embrittlement. Fortunately, none of these failures have contributed to a flight malfunction, all of them have occurred such that corrective actions could be taken to insure safe flights.

This report presents a brief account of specific failures that have occurred from this cause, a discussion of three related, but markedly different in character, aspects of hydrogen embrittlement and the status

of research programs that have been instituted to study this problem. Certain corrective actions that have been taken with respect to hardware or process changes are described. The three aspects of embrittlement considered are as follows:

1. High pressure hydrogen gas effects
2. Embrittlement by cleaning, electroplating, and pickling processes
3. Embrittlement of titanium by formation of titanium hydride.

#### THE EFFECT OF HIGH PRESSURE HYDROGEN ON VARIOUS METALS

Within NASA, studies in this area were begun as a result of failures in several large high pressure storage vessels for hydrogen gas. The histories of these failures and problems with related hardware are summarized in a report by McPherson and Cataldo [1]. Although it has been long recognized that very high pressure hydrogen will embrittle certain metals, the excellent experience with hydrogen storage at 3000 psi, normally used in smaller pressure vessels, gave confidence that storage at 5000-6000 psi would not be a problem. Therefore, when a large storage tank at Aerojet General Corporation developed a leak at a particular welded nozzle inlet in 1964, there was no great concern. But as similar failures occurred repeatedly, culminating in a failure through the cylindrical side wall of such a vessel, attention was directed toward an investigation of the hydrogen embrittlement potential under these high pressures.

These early failures occurred in vessels with laminated cylindrical sections, some with up to 22 layers, 0.289 inch thick, made with type 1146a steel and solid, forged heads of A225-B steel. A sketch of such a vessel is shown in Figure 1. The leaks were in the circular weldments where the 1-inch nozzles were inserted. A stress analysis indicated that the normal working stress plus the anticipated residual stresses may have been sufficient to result in failure. Also, fatigue due to the many pressure cycles used, could have contributed to failure in this area. However, since similar vessels of this design were known to have experienced long and satisfactory service histories with gaseous nitrogen, at 5000-8000 psi, the hydrogen pressurant was suspected as being the factor which contributed most to the leakage. In those particular vessels, however, the welded ports were replaced with a mechanical closure. One of the 1146a vessels was replaced in the hydrogen system with a vessel made of A517-F (T-1) steel. This fully stress relieved vessel was intended for use at 5000 psi; after ten pressure cycles, the vessel failed with an audible crack, although not catastrophically.

Leakage through the innermost shell egressed through weep holes drilled into each of the covering layers. Subsequent disassembly of this vessel revealed a considerable number of surface cracks in the welds of the shells. Two other T-1 steel vessels, which had not been in hydrogen service, were inspected and cracks were discovered in both of these also, although the cracks were not through the thickness of the shell. Thus, again, the matter of the influence of hydrogen was questioned.

At the Mississippi Test Facility of the Marshall Space Flight Center, in the meantime, three four-layered T-1 steel vessels were installed for hydrogen gas service at 6300 psi. These particular vessels did not have inspection ports; therefore, it was not positively known that cracks were present before they were put into service. On the second pressure cycle, one vessel failed at 5850 psi and leaked through the outer shell weepholes. Upon subsequent disassembly, cracks were found penetrating the 1-inch thick inner shell; all were associated with longitudinal welds. More recently, three identical vessels at that facility have been modified to install manways in the heads for inspection, and all three were found to contain surface cracks up to 1/4 inch deep. The majority of these cracks were in areas where tack welds had been used during initial fabrication.

When failure occurred in these vessels while in hydrogen service, hydrogen gas was released through small weep holes at a very high velocity. Although no ignition of the hydrogen occurred, there are numerous cases where vented hydrogen has ignited without any intended energy source. A study of critical factors for ignition under such venting conditions has not been made, but is fortunate, from the safety standpoint, that there was no ignition in the cases cited.

After the first T-1 steel vessel failure, the MSFC initiated a program at Rocketdyne, Canoga Park, California, to investigate the influence of high pressure hydrogen on a variety of alloys, principally those in common use for large storage tanks, but including also all those materials used in rocket engine hardware in both liquid and gaseous hydrogen systems. This work is described in a recent paper by Walter and Chandler [2]. Some of the alloys evaluated are listed in Table I in descending order of the influence of 10,000 psi hydrogen on the notch strength ( $K_t = 8$ ). This table is quite interesting in many respects; the reduction in notch strength is generally inversely related to the ambient yield strength of the material, but there are significant exceptions. For example, the A-286 alloy has a relatively high yield strength, but an apparent low sensitivity to the hydrogen. The best alloys are the aluminum alloys, copper, and stabilized stainless steels. Most of the commonly used storage vessel steels are grouped rather closely together by this ranking system; therefore, the selection of a material for a storage vessel material must be based primarily upon those factors in the design and fabrication that would permit a minimum



of as-fabricated surface defects, sound welds, and uniformly stressed material. Current technology in the fabrication of T-1 steel is greatly improved over that of several years ago; it is doubtful, however, that general commercial practices are such that T-1 steel can be fabricated with the resulting high quality necessary to provide sufficient confidence for safe operation with hydrogen. For high pressure hydrogen service, the data generated to date dictate that careful attention be paid to the surface finish of the material in contact with the hydrogen. Small surface cracks, in particular, must be avoided. A seamless, rather than a welded vessel, is preferred, simply from the standpoint of having fewer surface defects. However, a welded vessel is completely satisfactory provided good fabrication techniques are used and thorough quality control measures insure that welds have as few discontinuities as possible. Recent procurements of hydrogen storage vessels within NASA have included a new specification prepared by the Lewis Research Center [3].

Listed also in Table I is an alloy that gave rather surprising results, based on previous evaluations of low temperature strength and ductility, fracture toughness, and stress corrosion resistance. This alloy is Inconel 718. The particular sample of material evaluated had a yield strength of 185 ksi, yet in industry practice, the alloy is often used at somewhat higher yield strengths and the strength loss would be expected to be even greater in hydrogen under these conditions.

Recently, fracture toughness of Inconel 718 in hydrogen gas, at pressures as low as 1000 psi, has been evaluated by The Boeing Company, Seattle, and very low values were obtained. Battelle has made limited fracture toughness evaluations at temperatures as low as -100°F and obtained noticeable reductions of strength in this alloy. Within NASA, some material changes have had to be made recently in small pressure bottles previously made from Inconel 718. Other applications are being evaluated.

Failures in large hydrogen storage vessels, to date, have not proven conclusively that the hydrogen gas was the sole influencing factor. All of the failures have been associated with areas where very high residual stresses existed or where poor welding practices had been used. On the other hand, the failure of a number of hydrogen pressure gauges [1] was the result of the use of a material not suitable for this type of hydrogen service. The research work completed to date provides a fair assessment of the effects of high pressure hydrogen, and allows us to make better materials selections and establish safer design principles for hydrogen systems. Some of these research studies have been designed to evaluate the hydrogen compatibility of specific materials, some already in use in hydrogen systems; other studies are being made to investigate the more basic reaction mechanisms. Refined data, that would allow more economic, yet safe, designs in high pressure storage systems, are needed.

## EMBRITTLEMENT OF TITANIUM BY THE FORMATION OF TITANIUM HYDRIDE

In late 1966, during a preflight test of a Saturn launch vehicle third stage, an explosion occurred which completely destroyed the stage. Ultimately the explosion was traced to a Ti-6Al-4V helium pressure bottle which ruptured prematurely, causing secondary rupture of the stage propellant tanks.

An extensive metallurgical examination of the remains of this particular titanium bottle disclosed that (1) the bottle was welded with commercially pure (CP) filler wire rather than the specified Ti-6Al-4V filler, (2) the welds contained considerable amounts of titanium hydride phases, and (3) these hydride phases had diffused and segregated at the CP metal--parent metal interface and resulted in a relatively wide and extremely brittle zone. Subsequently, an extensive investigation was undertaken to determine why such quantities of hydrides formed in this case. Although CP wire was used mistakenly by the fabricator of these particular vessels, it is generally accepted as a suitable filler for Ti-6Al-4V alloy, and no previous problems had been reported with actual hardware. It was found that the thickness of the weldments in this bottle was such that multiple (seven to ten) weld passes were required and, consequently, little dilution of the filler and the parent metal occurred. This difference in composition, the tendency for hydrogen absorption in alpha titanium to be different than that for beta titanium, and the stress relief treatment used subsequent to welding appeared to satisfy the correct combination of factors to cause the formation of hydrides in the fusion zone. Figure 2 shows a half sphere of the bottle which failed and the complete fracture in the weld interface. Figure 3 is a cross-section view of the fracture and micrograph of the interface area showing the band of titanium hydride in a small section of the joint which did not rupture.

Since this particular pressure bottle had passed a proof test previously at a higher pressure than the final burst pressure, it became apparent that the hydride formation was not stable and had a deteriorating effect with respect to time, temperature, and applied or residual stress. As a result of laboratory evaluations made in connection with this investigation, a number of other observations were made as follows:

1. Hydrides are generally not apparent in the as-welded condition when Ti-6Al-4V is welded with CP wire. Small isolated precipitates may be located, but not in significant amounts.

2. Hydrides in various amounts generally always result from 1000°F stress relief treatments for 1 to 2-1/2 hours; small precipitates will tend to grow during the heat treatment.

3. The rate of cooling from 1000°F affects the amounts of hydrides formed; the slower the cooling rate the more dense the hydride formation at the weld interface.

4. Hydrides produced by a 1000°F stress relief can be partially redissolved by a 48-hour treatment at 212°F.

5. Various surface treatments can influence the amount of hydrogen absorbed and, consequently, the amount of hydrides formed. A clean surface produced by pickling, for example, will be less inhibiting than a mill scaled or oxidized surface.

6. Welding with CP wire so as to affect good dilution and maintain a high aluminum content reduces the tendency for hydride formation. Hydrides are not usually formed in thin sheet weldments due to the high dilution affected.

7. Welding with Ti-6Al-4V filler wire avoids the formation of hydrides.

8. The rate and amounts of precipitated hydride phases are dependent upon (1) dilution, (2) amount of absorbed hydrogen, (3) temperature, (4) time, and (5) stress.

During the course of this investigation, a survey of related research was made. Most previous work has concerned the study of titanium exposed to hot hydrogen gas, or other high temperature reactions. It is generally accepted that the natural oxidized surface protects titanium from extensive embrittlement at ambient temperatures. While some experiments have seemed to confirm this, from the practical viewpoint, it seems judicious to determine more exactly the conditions necessary for complete immunity, particularly in the case of weldments and in cases where the oxide surface may be momentarily destroyed. For example, a recent case was reported in which a small titanium hydrogen storage vessel failed at a point where screw threads engaged; apparently, the oxide coating was destroyed due to thread friction, and the friction energy created during vibrational movements in service was sufficient to cause a severe hydrogen reaction from the gas retained at ambient temperature. The surface layers of the threads were converted into hydrides, and they were essentially powdered by the reaction (see FIG 4). Some recent work pertinent to titanium-hydrogen reactions of this type has been reported by Williams and Maykuth [4] and work is currently in progress at McDonnell Douglas Company, NAS8-21470 [5] to study the effects of hydrogen on unprotected titanium alloy weldments.

Based on the data available at this time on titanium-hydrogen reactions, the use of titanium for hydrogen gas pressure vessels is not recommended. Likewise, the use of commercially pure filler metal

to weld alloyed titanium should be avoided. Insufficient data are available to define triggering mechanisms for titanium-hydrogen reactions. Where current applications of titanium in hydrogen systems are made, it is advisable to institute periodic inspections to assure that surface reactions have not occurred.

#### HYDROGEN EMBRITTLEMENT FROM VARIOUS CLEANING, PICKLING, AND ELECTROPLATING PROCESSES

Other ways in which hydrogen can be introduced in metals include heat treating operations, service environments, cleaning and pickling with acid solutions, and electroplating processes. The latter of these is perhaps the most commonly encountered and is of general concern since most high strength steels require electroplates for corrosion protection.

Several years ago, some studies at MSFC showed that specimens of 4340 steel, cadmium plated and baked (375°F for 24 hours) failed in less than 200 hours when loaded to stresses of 60 percent of their notched-bar tensile strength. In MSFC sponsored research at Battelle (NAS8-20029), considerable work has been done in the study of the embrittling effects of hydrogen through such processing techniques. This work has included three broad phases of study: (1) a determination of the relative susceptibility of a variety of alloys and a study of the embrittling effects of conventional pickling, cleaning, and electroplating of those alloys that were susceptible to embrittlement, (2) an investigation of the extent of embrittlement resulting from so-called "low-embrittling" or "non-embrittling" cleaning, activating, and electroplating processes, and a study of the effects of hydrogen embrittlement relief treatments, and (3) a study of the effects of various inhibitors for reducing hydrogen absorption during acid pickling or electroplating.

In the first phase of this study, the relative sensitivities of a selected group of materials to hydrogen embrittlement were determined by continuous cathodic charging of tensile specimens under a sustained tensile stress. If the smooth (unnotched) specimens sustained an applied tensile stress of 80 percent of their respective yield strengths for 200 hours or more without failure, they were considered to be insensitive. Those that failed in less than 200 hours were classified "sensitive". Several alloys that did not fail this test are listed in Table II. These particular alloys and their respective strength levels were selected for evaluation based on current applications in aerospace hardware. For those alloys that were classified as "susceptible", work was devoted to determining the minimum hydrogen content required for embrittlement under continuous charging. This was done by decreasing the severity of cathodic charging (under constant tensile stress) until the embrittling conditions were defined. Hydrogen analysis was then

made on specimens charged under these limited conditions. Results of these tests showed that the alloys could be arranged in groups according to their degree of susceptibility to embrittlement, as shown in Table III. The alloys within each of the four groups listed showed little significant difference in sensitivity.

The alloys evaluated contained different amounts of hydrogen under conditions that produced failure, but there appeared to be little correlation between the average hydrogen content of the alloys under limited charging conditions. The observation suggests that the alloys have significantly different tolerances for the amount of hydrogen required to produce failure and hydrogen distribution within a sample is a more important factor in hydrogen embrittlement than is the average hydrogen content of a sample.

The studies show that conventional cleaning, pickling, and electroplating processes can introduce sufficient hydrogen to cause failure even in mild steel alloys. Notched tensile specimens were loaded to an applied stress of 90 percent of their respective notched bar tensile strengths and the time required for fracture to occur was measured.

The delay time indicated the relative severity of embrittlement. The alloys evaluated by this technique are listed, in order of increasing degree of embrittlement, as follows: 18 Ni maraging steel, H-11 steel, 8740 steel, 4130 steel, and 4340 steel.

In the second phase of this study, H-11, 4340, and 18 Ni maraging steels, all in the 260 ksi strength level, were studied. The test procedure previously described was used to evaluate embrittling tendencies of selected cleaning, pickling, and electroplating processes.

Some observations noted in these evaluations were as follows:

1. None of the steels were significantly embrittled by conventional processing in an anodic alkaline cleaner, an anodic acid cleaner, or a soak type alkaline cleaner. But, 4340 steel was embrittled by an inhibited HCl pickling bath; H-11 and 18 Ni maraging were not.
2. Electroplating in a Watts-nickel bath introduced sufficient hydrogen to cause failures in 4340 and H-11, but not in 18 Ni maraging steels. Electroplating in a hard-chromium bath embrittled all three alloys. The amount of hydrogen introduced in chromium plating was greater than that introduced in severe cathodic charging.

An evaluation of the effectiveness of various baking treatments for relieving hydrogen embrittlement, as measured by the sustained load test, in plated specimens of selected alloys is given in Table IV. Results of

hydrogen analyses of the specimens prior to and subsequent to baking indicate that, generally, some hydrogen was released during the baking treatment; the data were not sufficient to establish any trend or to indicate significant relationships between alloys, but the type of electroplate did influence the amounts of hydrogen removed from the individual specimens.

An interesting consideration in the results of this work was that very recent attempts to induce hydrogen embrittlement in a second heat of 4340 steel were unsuccessful. This casts considerable doubt on any attempt to classify a particular alloy or to rank a series of alloys. This may indicate that minor compositional differences or strength levels, within the 4340 specification, could cause or eliminate serious hydrogen embrittlement problems, since the earlier work had shown 4340 to be one of the most susceptible alloys. This apparent difference has not yet been investigated thoroughly.

Based upon the results of all of the experiments to date, using the test procedures described, the following conclusions can be made:

1. Ti-6Al-4V, Inconel 718, Waspaloy, Rene' 41, and U-212 alloys were not susceptible to embrittlement by the processes evaluated.
2. Among the high strength steels, 4340 steel was the alloy most affected by the cleaning, pickling, and electroplating processes. Baking treatments reduced the severity, but no relief treatment attempted completely eliminated failures in this alloy.
3. Chromium plating was the most embrittling of any of the plating processes evaluated.

Those processes that will produce the least amount of surface reaction hydrogen are preferred to reduce possible hydrogen embrittlement; however, the results of this study has shown that, to date, no method of electroplating has been found that does not produce some degree of hydrogen embrittlement on certain alloys, such as the high strength alloy steels.

## DISCUSSION

Based on these evaluations and a review of classic studies in hydrogen-metal reactions, it appears that several undesirable events are caused by the entry of atomic hydrogen into steels and other metals and alloys. The source of the hydrogen is not necessarily related to the effects, but must be considered from the practical standpoint. Large quantities of hydrogen may cause a loss of ductility of a metal,

or if hydrogen accumulates in localized areas, internal bursts or blisters may occur. In some circumstances, hydrogen will react with the metal or alloy phases to form brittle compounds that may result in brittle fractures at applied stresses far below the normal yield strength or design stress of the material.

The various mechanisms of hydrogen reactions in the three subjects discussed in this review are probably sufficiently different to warrant some distinction. Where high pressure hydrogen is involved, the hydrogen entry into the metal is possible where the molecular hydrogen is dissociated into atomic hydrogen by the catalytic reaction with fresh metal surfaces. There is also the consideration that atomic hydrogen may be formed by the localized energy released by microcracking or in slippage in the metal. This atomic hydrogen enters the lattice of the metal and such entry is strongly influenced by temperature, lattice defects, and metals in the process of transformation or under stress. Such conditions provide the energy necessary for the endothermic process of dissolution of the hydrogen into the metal, either as interstitial solid solution or metal-hydrogen compounds on the basis of ionic bonding. Thus, the embrittling compounds or conditions are formed. The kinetics of lattice defects and hydrogen movements seem to be a fruitful area to be investigated.

The titanium-hydrogen reaction has had considerable investigation. The major influence in the case cited here is the difference in hydrogen solubility of alpha as contrasted to beta titanium. The commercially pure alpha alloy has no stabilizing elements such as the aluminum in the Ti-6Al-4V alloy. Aluminum belongs to a group of metals (Fe, Cu, Ni, Mo, etc.) in which the hydrogen is endothermically formed and dissolved as interstitial solid solution. Titanium, on the other hand, belongs to another group (such as Zr, Ta, Nb, etc.) in which hydrogen is found in the form of positively charged ions. Conditions causing hydrogen migration and the formation of titanium hydride have not been completely defined, although it is accepted generally that the Ti-6Al-4V alloy has sufficient aluminum to provide adequate solubility of hydrogen and the small amounts of hydrides formed are inconsequential. Migration mechanisms have been postulated and studied under various influencing conditions, but the triggering circumstances are far from being well enough defined to confidently predict limiting alloy compositions or to design weld filler alloys to control such mechanisms.

It seems that, regardless of the basic metal-hydrogen reaction mechanism or mechanisms that may take place, the application viewpoint must be one of caution. The resistance of a particular alloy to hydrogen damage under one set of conditions does not necessarily appear to apply for another. The designer must be especially careful where weldments are used, since new alloys and alloy phases may be formed in weldments that could be hydrogen sensitive. Additionally, weldments may entrap

pockets or narrow bands of hydrogen concentrations which are not readily detected, and subsequent hydrogen diffusion can take place even at relatively low temperatures, thus deterioration becomes time dependent.

The solution most often considered for eliminating hydrogen problems is to protect the metal in the first place. Where this cannot be done, techniques to drive out the hydrogen before it can do damage must be employed. There may be other approaches that have not been applied widely in practice, some of which have been explored briefly by some investigators.

#### NASA CORRECTIVE ACTIONS

As a consequence of the problems discussed here and the evaluation of data generated in the research programs described, various actions have been taken by MSFC and other NASA Centers to minimize the possibilities of hardware failures from hydrogen embrittlement.

1. In the case of high pressure effects, the following actions have been taken:

a. All high pressure hydrogen vessels have been surveyed with respect to possible safety hazards associated with their use. In some cases, additional safety precautions have been taken.

b. Selected vessels have been withdrawn from hydrogen service where the material and/or design have indicated some marginality.

c. Pressures in vessels have been reduced, particularly for long sustained pressure storage times.

d. A new specification for future pressure vessels has been prepared (SNPO-C-3, "Specification for High Pressure Gas Vessels") by the Space Nuclear Propulsion Office, LeRC.

e. Vessels with suspected defects have been inspected internally and appropriate repairs made. Vessels without inspection manways are being modified to install such manways to permit periodic future inspections.

2. In the case of titanium hydride problems, the following actions have been taken:

a. All Saturn Apollo titanium propellant and/or gas pressure vessels have been surveyed to evaluate the possible embrittlement of such vessels due to titanium hydride formations. These evaluations



included the assessment of fabrication processes, design parameters, environmental conditions, and a careful inspection of weldments in selected vessels with an eddy-current technique developed to indicate the relative alloying obtained between the base metal and weld filler material.

b. Manufacturing processes are more carefully controlled to assure that commercially pure filler wire is not used for thick titanium weldments and that good alloying is effected between the filler and the base metal in thinner materials.

c. All contractors are required to maintain log books to account for pressure cyclic histories on all titanium pressure vessels in the Saturn Apollo system.

d. A NASA directive (APD-23) has been issued to provide more careful control over all fluids coming in contact with pressure vessels with respect to compatibility of the fluid and/or the specific process used.

3. In the case of embrittlement resulting from cleaning, plating, and pickling processes, the following actions have been taken:

a. A specification for cadmium plating (MSFC Drawing No. 10419960) was issued which increases the baking time over that required in QQ-P-416 (Federal Cadmium plating specification).

b. MSFC-SPEC-250, "Protective Finishes for Space Structures and Associated Flight Hardware", was prepared which contains several provisions for controlling and preventing hydrogen embrittlement. This specification states, "For cadmium plating of steel exceeding 220 ksi (Rockwell C-40) use vapor plating process conforming to MIL-C-8837 or electroplating may be used when approved in accordance with MIL-S-5002".

c. Numerous contractor process specifications have been amended to improve the baking requirements and limit the hardness of various alloys subject to embrittlement.

d. Very high strength steel fasteners (such as 260 ksi H-11) are prohibited from use in spacecraft hardware.

#### CONCLUSION

Hydrogen-metal reactions, under guise of various applications, have accounted for extremely costly and schedule affecting problems in Saturn-Apollo hardware and associated ground support equipment. Although

these problems have been fixed in various ways, the investigations conducted have pointed out various avenues wherein research is yet needed in this area. The logical approach has been taken. As a first priority, attempts have been made to make suitable materials and/or design changes where necessary, and to utilize processing techniques which minimize the hydrogen problem. As a second priority, additional basic research has been undertaken to elucidate the hydrogen-metal reaction mechanisms and the environmental conditions which influence such reactions.

Until such time as data are developed to permit otherwise, the materials selection specialist and designer are cautioned to take a conservative approach where hydrogen applications are involved.

#### REFERENCES

1. McPherson, W. B.; and Cataldo, C. E.: Recent Experience in High Pressure Gaseous Hydrogen Equipment Operated at Room Temperature, paper presented at ASTM-ASME Symposium on Effects of Gaseous Hydrogen on Metals, 1968 Materials Engineering Congress, Detroit, Michigan, October 13-17, 1968.
2. Walter, R. J.; and Chandler, W. T.: Effect of High Pressure Hydrogen on Metals, paper presented at ASTM-ASME Symposium on Effects of Gaseous Hydrogen on Metals, 1968 Materials Engineering Congress, Detroit, Michigan, October 13-17, 1968.
3. Specification Number SNPO-C-3, Revision 1, dated November 1967, Specifications for High Pressure Gas Vessels, Space Nuclear Propulsion Office, Lewis Research Center, NASA, Cleveland, Ohio.
4. Williams, D. N.; and Maykuth, D. J.: Reaction of Titanium with Gaseous Hydrogen at Ambient Temperature, DMIC Technical Note, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio, February 4, 1966.
5. McDonnell Douglas Company, Missile and Space Systems Division, Effects of Hydrogen on Unprotected Titanium Alloy Weldments, NASA/MSFC Contract NAS8-21470.

TABLE I. ARRANGEMENT OF MATERIALS IN ORDER OF PERCENT  
REDUCTION OF NOTCH STRENGTH IN 10,000 PSI HYDROGEN

<u>Alloy</u>	<u>Yield Strength</u> <u>ksi</u>	<u>Percent Reduction</u> <u>Notch Strength</u>
18 Ni 250 Maraging	248	88
17-7 PH SS	150	77
H-11	244	76
Rene' 41	163	73
4140	179	60
Inconel 718	182	54
Ti-6Al-4V (STA)	156	45
Nickel 270	22	30
HY-100	97	27
Ti-6Al-4V (Annealed)	132	25
A302	-	22
HY-80	81	21
304 ELC SS	24	13
A-517 (T-1)	109	11
Be-Cu	79	7
Ti (C.P.)	53	5
310 SS	-	3
A-286 SS	123	3
7075-T73	54	2
6061-T6	33	0
1100 Al	-	0
OFHC Copper	39	0
316 SS	64	0

TABLE II. MATERIALS NOT SUSCEPTIBLE TO HYDROGEN EMBRITTLEMENT  
BY ELECTROPLATING, OR PICKLING

- o Ti-6Al-4V
- o Inconel 718
- o Waspaloy
- o Rene' 41
- o U-212

TABLE III. METALS SUSCEPTIBLE TO HYDROGEN EMBRITTLEMENT

17-7 PH Stainless Steel	(200,000 psi)
AM-355 Stainless Steel	(180,000 psi)
18 Ni Maraging Steel	(200,000 psi)
AISI E 8740 Steel	(180,000 psi)
H-11 Steel	(260,000 psi)
H-11 Steel	(220,000 psi)
17-4 PH Stainless Steel	(200,000 psi)
4340 Steel	(260,000 psi)
4130 Steel	(180,000 psi)

TABLE IV. THERMAL TREATMENTS FOR HYDROGEN EMBRITTLEMENT RELIEF

Cadmium Plating

1. Baking 24 hours at 375°F - Satisfactory for bright or dull plated H-11 and 18 Ni maraging steel, but not for 4340. Satisfactory for bright Cd plated 4130 and 8740.
2. Baking 3 hours at 375°F - Satisfactory for dull Cd plated 4130 and 8740.

Watts Nickel Plating (Without Brightness)

1. Baking 24 hours at 375°F (or 2 hours at 600°F) - Satisfactory for H-11 and 18 Ni maraging steel.
2. Baking 24 hours at 375°F did not eliminate H<sub>2</sub> embrittlement in 4340 steel.

Chromium Plating

Baking 24 hours at 375°F (or 2 hours at 600°F) - Satisfactory for 18 Ni maraging steel but not for H-11 or 4340.

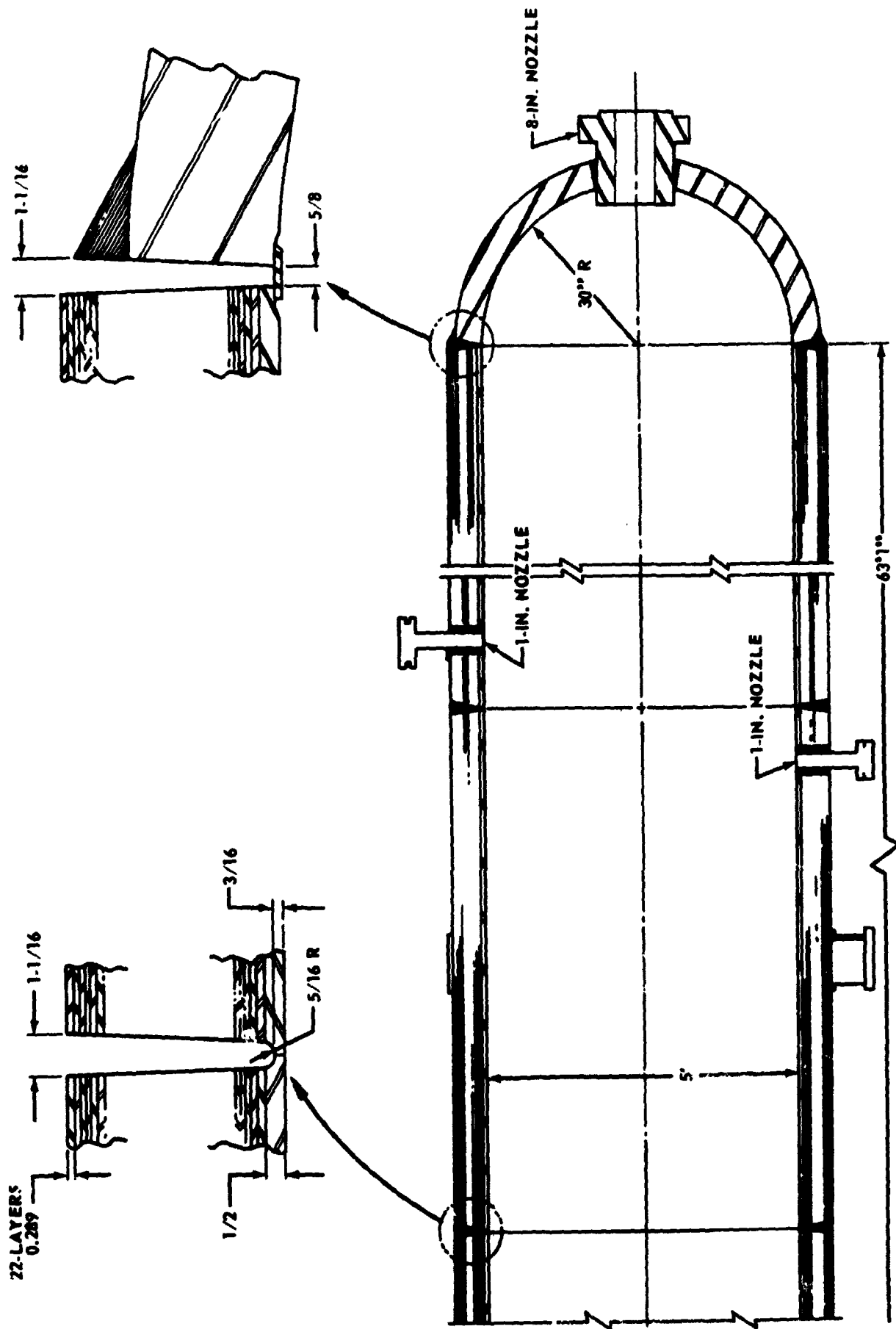


FIGURE 1. Sketch of Multiple Layer Construction for Pressure Vessel

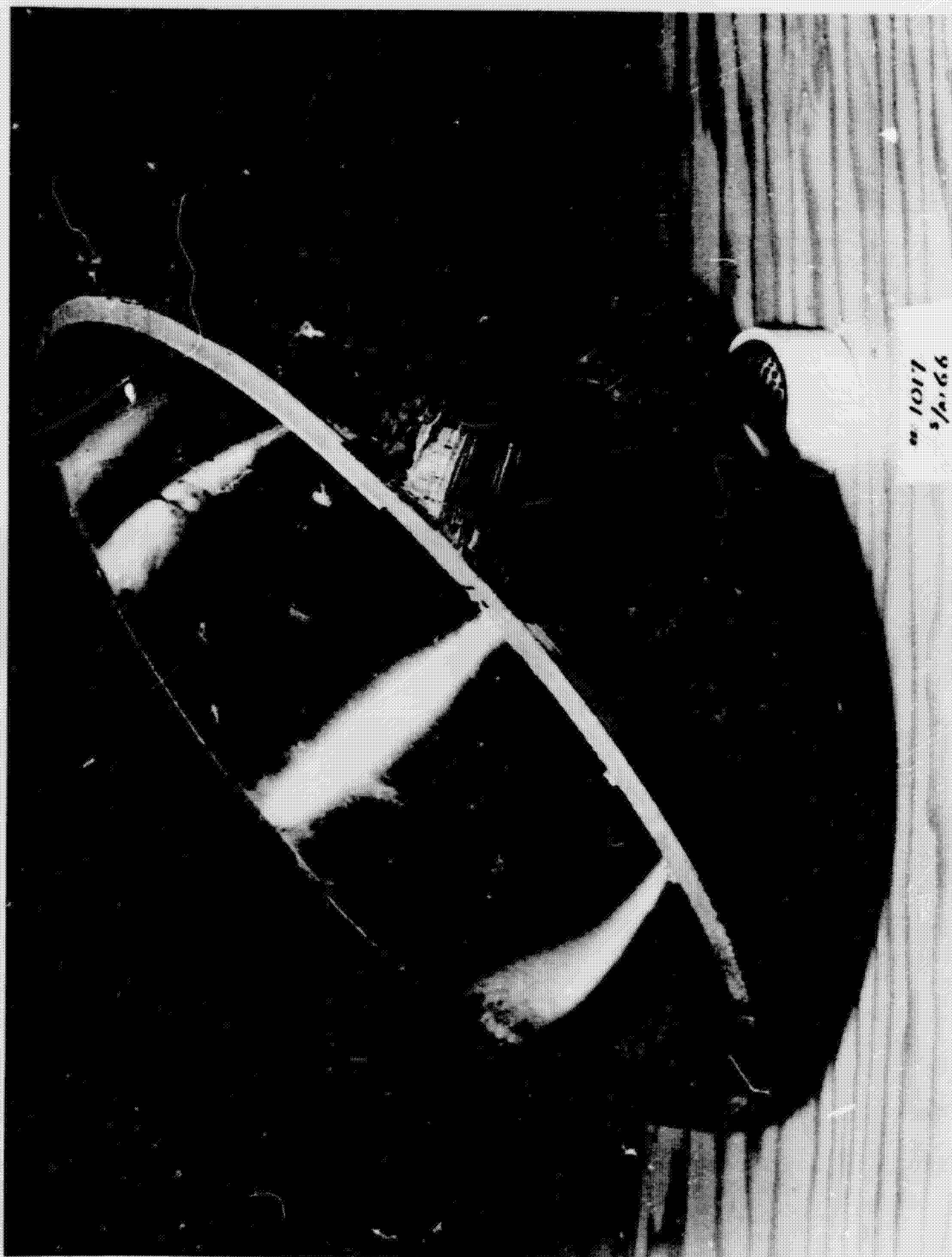


FIGURE 2. - Half Sphere of Fractured Titanium Helium Bottle



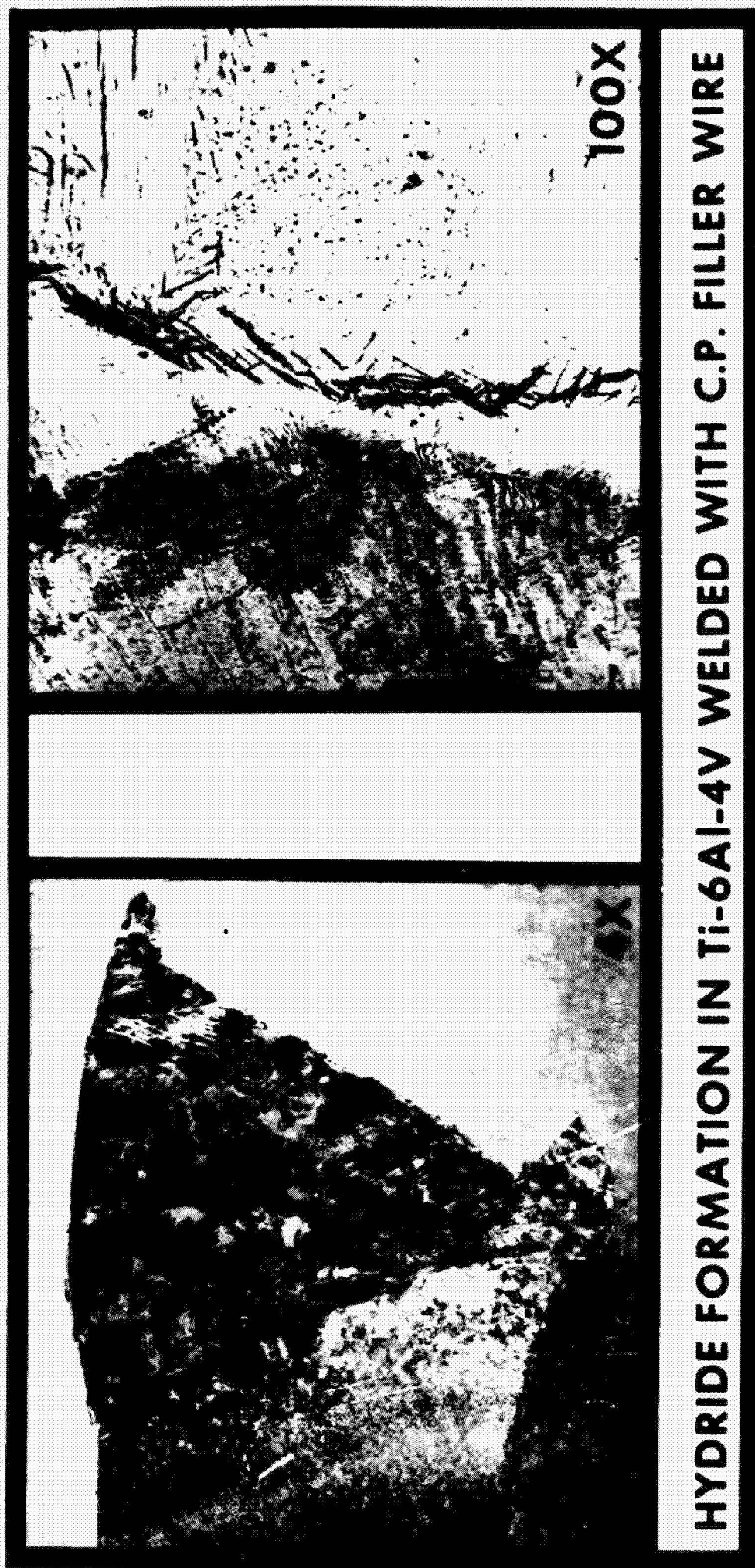
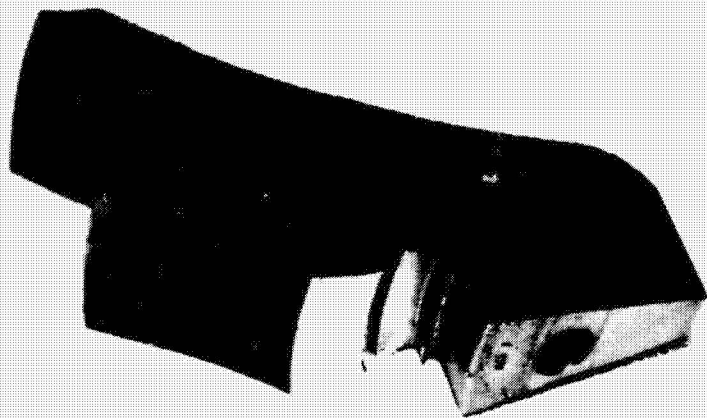


FIGURE 3





Cross-Section of Threaded Segment of Pressure Bottle



Cross-Section of Threaded Area

FIGURE 4

December 26, 1968

NASA TM X-53807

APPROVAL

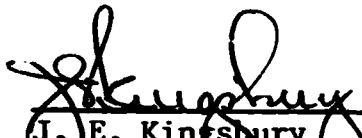
COMPATIBILITY OF METALS WITH HYDROGEN

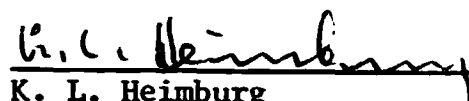
By

C. E. Cataldo

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

  
\_\_\_\_\_  
J. E. Kingsbury  
Chief, Materials Division

  
\_\_\_\_\_  
K. L. Heimburg  
Director, Propulsion and Vehicle Engineering Laboratory